Photovoltaic properties of DSSC with composite counter electrodes based on Pt and SLGO

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Abstract. Langmuir-Blodgett (LB) films based on graphene oxide were synthesized and studied. Structure and optical properties of the films are studied. At using of the films as counter electrodes in DSSC cells, it is shown that pure LB graphene oxide films, despite the advantages in electrotransport properties, have a rather high resistance. This is lead to the decreasing in the number of charge carriers injected into the semiconductor layer from the dye molecules, and in a complex decrease in the efficiency of solar cells. However, when LB films are deposited over the Pt layer, the electron transport characteristics of the counter electrodes are improved, which is manifested in an increase in the efficiency of solar cells compared to cells with a conventional Pt electrode.

1. Introduction

Graphene and its modified derivatives, like other nanostructures, show the dependence of properties on size and morphology. 2D-graphene shows different properties in comparison with its 1D form, i.e. carbon nanotubes. The 2D structure of graphene makes it more compatible with planar substrates, which can be a viable alternative for silicon substitution. In addition, the 2D structure of graphene layers and their atomic dimensions give them unusual properties [1]. High conductivity and a high ratio of surface area to volume are the most outstanding characteristics of layered graphene nanostructures [2]. In addition, it was shown in [1, 3] that graphene possesses a high specific surface area, high electron mobility and a higher oxidation potential than Pt, which is the traditional material used in dye-sensitized solar cells (DSSC). Due to the variety of existing forms of graphene, it is possible to improve the necessary parameters of the counter electrodes in solar cells. For example, reduced graphene oxide has surface lattice defects, which implies a higher catalytic activity than a completely reduced defect-free graphene [4, 5].

Given the transparency of the single- or multilayer graphene structure and its conductivity, and the fact that the cost of producing of graphene can be cheaper than for other carbon nanomaterials, makes it a very promising material in the production of photovoltaic devices.

There are several methods for obtaining graphene nanostructures. Typically, CVD technology, aerosol spraying and polyione assembling are used for deposition of graphene layers [6, 7]. Polyione assembling and CVD are complicated procedure, that requires additional preparation of substrates and

template for growing of graphene films. Furthermore, there is the problem of controlling of thickness of synthesized coatings, which is a negative factor.

Langmuir-Blodgett (LB) technique allows to control the thickness of films as well to predict the orientation of the particles within it. It means that the combination of possible variations in number of layers and the distance between the individual graphene sheets enable control not only the conductivity and resistance of the films, but also to adjust the surface area of the film. This opens up the possibility of creating a highly efficient catalyst graphene layer with high conductivity for using in photovoltaic cells.

In this paper, the results of an investigation of the photovoltaic characteristics of DSSC with counter electrodes based on graphene oxide LB films and Pt are presented.

2. Experiment

For the preparation of LB films of graphene oxide (SLGO, Cheaptubes), dispersions in dimethylformamide (DMF) were used. The solvent (analytical grade) were purchased from Sigma-Aldrich and used without further purification. The concentration of SLGO in the solution is 0.03% by weight. Graphene solutions were processed for 60 minutes in an ultrasonic bath.

The investigated monolayers were formed by spreading from a solution in a Langmuir bath (KSV Nima). The isotherms of compression of graphene oxide monolayers at the water-air interface were measured and investigated. To stabilize the monolayer, it was held for 40 minutes. Deionized water purified using the AquaMax water purification system was used as a subphase. The specific resistance of water was equal to 18.2 MΩ/cm. The surface pressure was 72.8 mN/m at pH = 5.6 and temperature of 22 °C.

Measurements of the π-A isotherms showed that, the SLGO monolayer under compression passes from the gaseous to the liquid-stretched [8, 9] state at small volumes of the sprayed solution on the surface of the subphase. In this case, the surface pressure increases smoothly without the collapse of the monolayer. An increase in the number of particles in the monolayer leads to a shift of the π-A isotherm curve toward smaller areas, and the length of the gaseous and liquid phases in this case decreases. The value of the surface pressure was chosen for the transfer of films, when the monolayer is in a more condensed liquid state – at 8 mN/m. Solid films were deposited by the LB method according to the X-type transfer, since it was shown in [8, 10] that such films are more homogeneous in structure than films obtained according to the Z-type transfer. The rate of monolayer transfer was equal to 8 and 19 mm/min, and the compression rate of the monolayer was equal to 5 mm/min. For the deposition of SLGO films, glass plates coated with a FTO layer were used. 1 monolayer of graphene oxide was deposited on the substrates. For the layered films SLGO was deposited over the layer of Pt catalysts. The platinum catalyst was electrochemically applied from an ethanol solution of H_2PtCl_6 (Sigma Aldrcih).

The preparation and assembling of solar cells was carried out according to the procedure detailed in [11, 12]. To prepare of solar cells, glass substrates coated with a FTO layer (Sigma-Aldrich, surface resistance of ~ 10 Ohm/sq) were used. Blocking layer of TiO_2 was deposited on the surface of the FTO. Semiconductor films were prepared by the doctor-blading method. To prepare the films, TiO_2 with a nanoparticle size of 25 nm was used (Sigma-Aldrich). The thickness of the resulting films was measured by the SEM (Tescan Mira-3) and was equal to 10 – 12 microns. Sensitization of semiconductor electrodes with ruthenium dye (N719, Sigma Aldrich) was carried out by immersion of TiO_2 films in an ethanol dye solution with concentration equal to 4×10^{-4} mol/l for 20 hours. Before measurement, the films were kept in an oven at a temperature of 80 °C for at least of 1 hour. The number of adsorbed dye molecules in all samples was controlled by the change in the optical density of the solutions before and after sorption.

The current-voltage characteristics of DSSC were measured with Solar Cell Tester CT50AAA (Photo Emission Tech. Inc., USA) under illumination of the xenon lamp with light intensity of 100 mW/cm^2. The measurements were performed at room temperature in photovoltaic mode. From the obtained values of the open circuit voltage, short-circuit current and fill factor, the efficiency of the

cells was determined. Electric transport properties of solar cells based on porous titania films with various opposite electrodes were studied by measuring the impedance of an electrochemical cell. The measurements were carried out on an Z-500PRO impedance meter (Elins, Russia) under irradiation of cells with standard simulated solar radiation (Air Mass (AM) 1.5). The amplitude of the applied sinusoidal signal was 20 mV, and the frequency varied from 1 MHz to 100 MHz.

3. Results

SEM images of the obtained LB films are shown in Figure 1. It can be seen from the Figure 1 that the number of particles with a large number of layers, as well as areas with wrinkles and folds, is small in SLGO LB films. When analyzing the area of the of the LB film on the surface of the substrate, it was found that the monolayer occupies about 80 % of the total area.
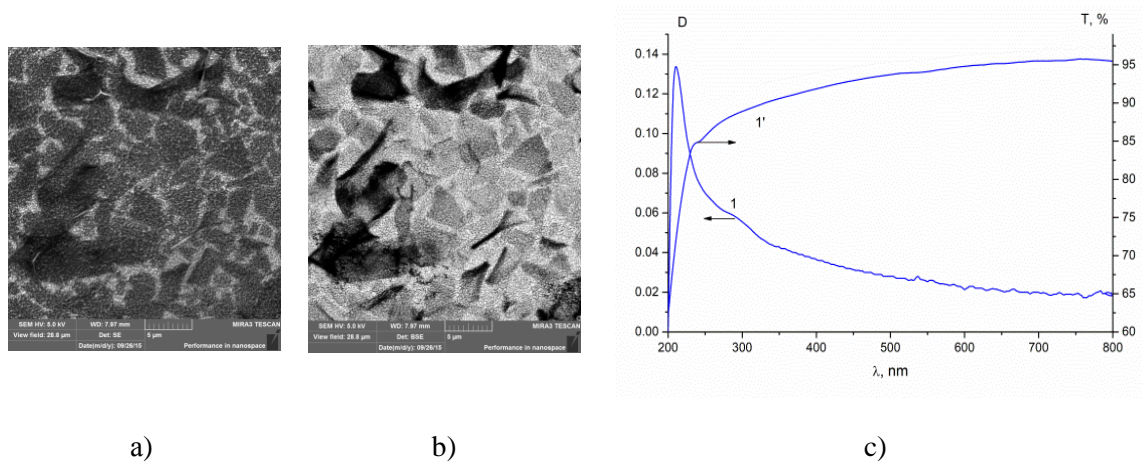

a)   b)   c)

Figure 1. SEM images of the graphene oxide LB film (*a, b*). Image (*b*) was obtained with the reflected-electron sensor. (*c*) Absorption (1) and transmission (1') spectra of graphene oxide LB films.

The maximum of the absorption spectrum of the LB film exhibits at 230 nm with an weak shoulder about 300 nm (Figure 1*c*). The transparency of the films in the visible spectral range varies from 90 to 95 %.

The measured I-V characteristics are shown in Figure 2 and in Table 1. As it was shown, the efficiency of the cells decreases when the graphene oxide LB films is used instead the platinum catalysts. Such a drop, first of all, is caused by a decrease in the value of the cell fill factor by 4 times. Reducing the efficiency of solar cells using graphene is a well-known fact [13, 14].

In addition, a large resistance was recorded for the cell with the SLGO electrode, compared to the value typical for the traditional Pt electrode (Table 2). These parameters indicate the low electron transport properties of graphene oxide, despite its high photocatalytic activity. However, the use of composite layered electrodes Pt+SLGO allows to solve this problem. As can be seen from the Table 1, for this type of electrode, the efficiency values is higher than for a cell with a platinum catalyzing layer.

Thus, as shown by the results of measurements, the use of graphene oxide films in combination with a platinum catalyst is more promising for photovoltaic cells.
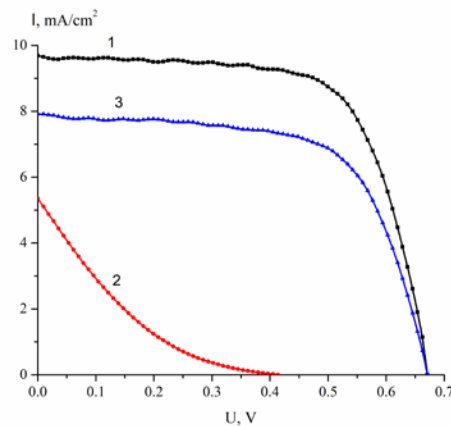
Figure 2. I-V characteristics of solar cells with different counter electrodes: 1 – Pt; 2 – SLGO;

3 – Pt+SLGO.

Table 1. Photovoltaic parameters of solar cells.

Counter electrode	U_{oc}, V	J_{sc}, mA/cm^2	FF	Efficiency, %
Pt	0.67	9.7	0.67	4.4
SLGO	0.41	5.3	0.13	0.3
Pt+SLGO	0.67	7.9	0.65	3.4

Figure 3 shows the hodographs for solar cells with different electrodes. The measurements showed that the magnitude of both the real and imaginary part of the resistance of the electrochemical cell increased significantly when using graphene oxide. The cell resistance is reduced to 40 Ohms and 45 Ohms for platinum electrode and a Pt + SLGO composite electrode respectively.
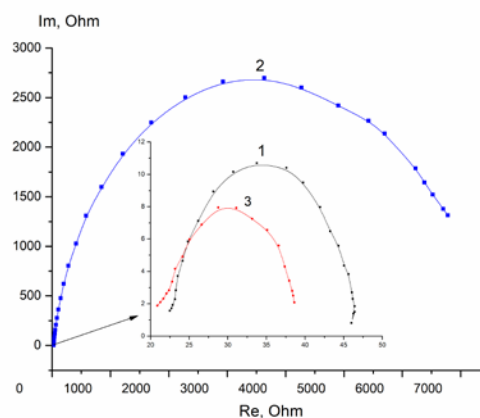

Figure 3. The impedance hodograph curves of DSSC with different electrodes: 1 – Pt; 2 – SLGO;
3 – Pt+SLGO.

Based on the hodographs obtained, the effective diffusion coefficient of electrons D_{eff}, the effective recombination rate k_{eff}, the effective electron lifetime τ_{eff}, the resistance of electron transport in a titanium dioxide film R_w, the charge transfer resistance R_k, associated with electron recombination, were calculated from the central curve of the impedance spectra [15, 16] (Table 2).

It was shown, that in graphene oxide films, the diffusion length of electrons is 2 orders of magnitude higher than in platinum electrodes.

Table 2. Electrotransport parameters of solar cells.

Counter electrode	D_{eff}	$k_{eff,}$ s^{-1}	$\tau_{eff,}$ s	$R_{k,}$ Ohm	$R_{w,}$ Ohm
Pt	3.3×10^{-5}	28.7	0.03	17.5	20.5
SLGO	1.4×10^{-3}	3.3	0.3	6980.0	22.5
Pt+SLGO	3.8×10^{-5}	22.4	0.04	24.5	20.0

However, R_k of these films is more than three orders of magnitude larger. This means, as indicated above, despite the advantage of graphene oxide as a catalyst in comparison with Pt, SLGO film resistance is greater with comparison to the traditional platinum electrodes which is expressed in high values of D_{eff} and τ_{eff}. This, in turn, is reflected in a decrease in the number of electrons injected into the semiconductor layer from the dye molecules, which do not have a time to reduce. As a result, a very small number of electrons will diffuse into the semiconductor, which is expressed in a decrease in the current values generated by the solar cells.

4. Summary
Thus, the conducted studies have shown that for photovoltaic cells the use of graphene oxide films in combination with a platinum catalyst is more promising. Graphene oxide LB films, despite the advantages in electrotransport properties, have a high resistance, which is a result in the decreasing of the number of charge carriers injected into the semiconductor layer from the dye molecules and in a complex decrease in the efficiency of solar cells.

Acknowledgments

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